I. REDUCTIVE CLEAVAGE OF DIOXOLONES BY THE GRIGNARD REAGENT

II. A VINYLOG OF 1,2-DIMESITYLACETYLENE GLYCOL: 1,2,5,6-TETRAMESITYL-1,3,5-HEXATRIENE-1,6-DIOL

BY

ALBERT ISRAEL RACHLIN

Sc.B. in Chem., Brown University, 1937

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1942

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ACKNOWLEDGMENT

The author is grateful to Professor Reynold C. Fuson for his kindly interest and invaluable assistance in the development of these investigations.

REDUCTIVE CLEAVAGE OF DIOXOLONES BY THE GRIGNARD REAGENT

Introduction

A good synthetic method for the preparation of mixed benzoins of the type ArCOCHOHAr′ has been the goal of many investigations. It appeared likely that the Grignard reagent would react with dioxolones to give the desired product provided that the reaction could be limited to the addition of one mole of the reagent. Experiment showed, however, that the reaction took an entirely unexpected course.

Discussion

The dioxolones were made by the general method of Audrieth and Sveda,[1] by condensing an α-hydroxy acid with acetone in the presence of sulfuric acid.

The reaction of *t*-butylmagnesium chloride with acetone-mandelic acid led to the formation of an acid which was identified by an independent synthesis as α-isopropoxymandelic acid. The highest yield was 57 per cent. Isobutylene was evolved. The isopropyl ethers of *p*-methylmandelic, *p*-bromomandelic, α-mesitylglycolic, lactic and α-hydroxyisobutyric acids were also prepared from the corresponding dioxolones in yields of 66, 71, 80, 20 and 50 percent, respectively.

The reaction is a hydrogenolysis of the dioxolone ring. Attempts to effect the reduction of the acetone derivative of mandelic acid by other alkyl Grignard reagents were unsuccessful. In fact, the reduction could not be carried out by use of common reducing agents such as hydrogen over platinum or copper chromite,[2] the binary mixture ($Mg\text{-}MgI_2$),[3] the zinc-copper couple and aluminum isopropoxide.

The behavior of aryl Grignard reagents was influenced by the presence of ortho substituents. Phenylmagnesium bromide reacted normally with acetone-mandelic acid to form triphenylethylene glycol.[4] Mesitylmagnesium bromide caused the formation of an intractable oil. *o*-Tolylmagnesium bromide

caused the formation of a mixture of products which were identified as 1-phenyl-2,2-di-*o*-tolylethylene glycol, 1,1-di-*o*-tolyl-3,3-dimethyl-5-phenyldioxolane and *w*,*w*-di-*o*-tolylacetophenone. The glycol and the dioxolane were easily converted to the ketone by the action of mineral acids.

A VINYLOG OF 1,2-DIMESITYLACETYLENE GLYCOL: 1,2,5,6-TETRAMESITYL-1,3,5-HEXATRIENE-1,6-DIOL

Introduction

It has been shown that the hydrogenation of ∝-mesitylvinyl mesityl ketone proceeded in the 1,4 manner to produce 1,2-dimesityl-1-propen-1-ol.[5,6] Other reducing agents might be expected to behave similarly. Thus, the binary mixture (Mg-MgI_2), caused the bimolecular reduction of this ketone to form 1,2,5,6-tetramesityl-1,5-hexadiene-1,6-diol. The investigation involved a study of this diol and its derivatives.

Discussion

1,2,5,6-Tetramesityl-1,5-hexadiene-1,6-diol was shown to be a stable solid dienol. It formed a diacetate, indicating the presence of two hydroxyl groups. Ethanolic hydrogen chloride converted it to the keto form, 1,2,5,6-tetramesitylhexane-1,6-dione. The enolic modification was regenerated from the diketone by the action of ethylmagnesium bromide. Ozone failed to cleave the dienol. However, when oxygen was bubbled through an acetone solution of the compound, it was cleaved to mesitol and 1,4-dimesitylbutane-1,4-dione. The same reagent cleaved 1,2-dimesityl-1-propen-1-ol to mesitol, acetomesitylene and a small amount of mesitoic acid.

Potassium permanganate in acetone solution dehydrogenated the dienol to form 1,2,5,6-tetramesityl-2,4-hexadiene-1,6-dione, a yellow compound vinylogous with mesitil. Cleavage to form appreciable amounts of ∝-mesitylvinyl mesityl ketone occurred simultaneously. Lead tetraacetate gave the same results.

The yellow diketone could be reduced either with hydrogen over platinum or zinc and glacial acetic acid to give 1,2,5,6-

tetramesityl-1,3,5-hexatriene-1,6-diol. This compound, a vinylog of 1,2-dimesitylacetylene glycol, decomposed in the presence of air, reverted to the yellow diketone under the influence of hydrogen peroxide and decolorized sodium 2,6-dichlorobenzeneoneindophenol.[7] It formed a diacetate, the same compound being produced when the yellow diketone was reduced catalytically by the method of Thompson.[8] The triendiol was ketonized by the action of ethanolic hydrogen chloride, the product being 1,2,5,6-tetramesityl-3-hexene-1,6-dione. Ethylmagnesium bromide regenerated the trienediol from the diketone.

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VITA

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